

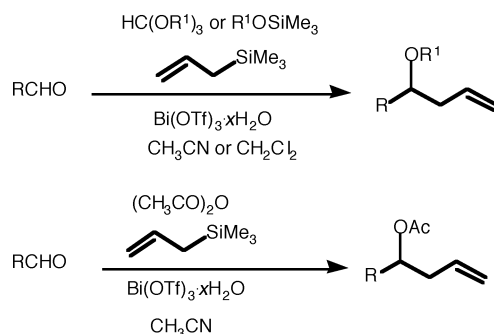
Bismuth Compounds in Organic Synthesis. A One-Pot Synthesis of Homoallyl Ethers and Homoallyl Acetates from Aldehydes Catalyzed by Bismuth Triflate

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Three one-pot methods for the conversion of aldehydes to homoallyl ethers catalyzed by Bi(OTf)₃·xH₂O (1 < x < 4) have been developed. The one-pot synthesis of homoallyl ethers can be achieved either by *in situ* generation of the acetal followed by its reaction with allyltrialkylsilane or by a three-component synthesis in which the aldehyde, trimethylorthoformate or an alkoxytrimethylsilane and allyltrimethylsilane are mixed together in the presence of bismuth triflate (0.1–1.0 mol %). In addition, a three-component synthesis of homoallyl acetates, which is achieved by reacting the aldehyde, acetic anhydride, and allyltrimethylsilane in the presence of bismuth triflate (3.0–5.0 mol %), has been developed. The use of a relatively nontoxic, easy to handle, and inexpensive catalyst adds to the versatility of these methods.

Introduction

Homoallyl ethers and homoallyl acetates are versatile functional groups amenable to further synthetic manipulation, and hence, their synthesis has attracted considerable attention. The allylation of acetals using organosilicon reagents is a useful method to generate homoallyl ethers, and hence, several catalysts have been used to effect this transformation. These include TiCl₄,¹ AlCl₃,² BF₃·Et₂O,² trityl perchlorate,³ diphenylboryl triflate,³ montmorillonite,⁴ Pb/Al,⁵ trimethylsilyl bis(fluorosulfonyl)imide,⁶ (CH₃)₃SiI,⁷ TMSOTf,⁸ TiCp₂(CF₃SO₂)₂,⁹

CF₃COOH,¹⁰ BiBr₃,¹¹ trimethylsilyl bis(trifluoromethanesulfonyl)amide [TMSNTf₂],¹² Sc(OTf)₃,¹³ indium metal,¹⁴ and Bi(OTf)₃·xH₂O.¹⁵ However, many acetals are not

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TABLE 1. Bismuth Triflate Catalyzed One-Pot Method for the Synthesis of Homoallyl Ethers Using Trialkylorthoformates

Entry	Aldehyde	Acetal Intermediate	Product	Time ^a (t ₁ , t ₂)	Yield ^b (%)
1	PhCHO			1 h, 10 min	75 ¹
2 ^c	PhCHO			1.5 h, 10 min	89 ²⁸
3	<i>p</i> -ClC ₆ H ₄ CHO			1.5 h, 15 min	83 ⁵
4	<i>p</i> -CH ₃ C ₆ H ₄ CHO			1 h, 10 min	71 ¹³
5				3 h, 15 min	77 ¹³
6 ^d	<i>m</i> -BrC ₆ H ₄ CHO			1 h, 45 min	72 ¹⁵
7				4 h, 15 min	64 ⁸
8	C ₉ H ₁₉ CHO			30 min, 10 min	72 ²⁹

^a t₁ refers to the time for the acetal formation step, and t₂ refers to time for the allylation step. ^b Refers to yield of isolated, purified product. Yields are not optimized. The purity of all products was determined to be 96–99% by ¹H and ¹³C NMR spectroscopy and GC analysis. Superscript against yield refers to literature reference for the product. ^c Only 0.1 mol % Bi(OTf)₃·xH₂O was used. The allylation proceeded without the need for additional catalyst. ^d Ethanol and HC(OEt)₃ were used in place of CH₃OH and HC(OMe)₃.

commercially available and must be synthesized from the corresponding aldehydes.¹⁶ In addition, most of these methods only report allylation of dimethyl or diethyl acetals which results in the formation of homoallyl methyl or ethyl ethers, respectively. Although the alkene moiety of homoallyl alkyl ethers can be easily transformed into other groups, alkyl ethers are somewhat inert and not amenable to easy synthetic manipulation. Another disadvantage of this approach is that many acetals have poor shelf lives. However, there are very few reports of one-pot syntheses of homoallyl ethers and homoallyl acetates from aldehydes.¹⁷ Further, many of these methods require the use of corrosive catalysts such as TMS triflate or expensive, highly moisture-sensitive and toxic catalysts such as Sc(OTf)₃. Recently, an environmentally friendly approach to the synthesis of homoallyl benzyl ethers, in which the acetal is generated *in situ* from the corresponding aldehyde using FeCl₃ as the catalyst, has been reported.¹⁸ With increasing environmental concerns,

the need for environmentally benign synthetic chemistry has assumed significant importance. According to the principles of green chemistry, synthetic methods should be designed to use substances that exhibit little or no toxicity to human health and the environment.¹⁹ In this regard, bismuth compounds have recently attracted considerable attention. Bismuth compounds are remarkably nontoxic,²⁰ and many bismuth reagents have proven to be versatile catalysts for a variety of organic transformations.²¹ The low toxicity of bismuth has earned it the status of a green element. Our continued interest in bismuth compounds, due largely to their remarkably low toxicity, low cost, and ease of handling, prompted us to investigate a bismuth(III) triflate catalyzed one-pot approach to the synthesis of homoallyl ethers and homoallyl acetates.²² A one-pot synthesis saves steps by eliminating the need to isolate the intermediate and thus minimizes waste. Herein we report the results of our studies leading

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to the development of three one-pot methods for the conversion of aldehydes to a variety of homoallyl ethers (Tables 1–3) catalyzed by bismuth(III) triflate. In the first approach (Table 1), the acetal was generated *in situ* and then converted to the corresponding homoallyl ether. The use of a nonaqueous workup eliminates an aqueous waste stream. The acetal was generated *in situ* by reaction of the aldehyde with trialkylorthoformate and the corresponding alcohol in the presence of 0.1 mol % $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$. The reaction progress was monitored by GC. After the aldehyde was consumed, the alcohol was removed under reduced pressure, and then acetonitrile, the corresponding allylsilane, and 1.0 mol % of the catalyst were added. It was found that this was more effective than having 1.0 mol % $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ in the beginning of the reaction. If the methanol was not removed prior to addition of the allyltrimethylsilane, no allylation was observed and the acetal intermediate was isolated. With a more nucleophilic silane such as methylallyltrimethylsilane (Table 1, entry 2), the reaction proceeded without the addition of the second portion of the catalyst. To the best of our knowledge, this is the first example of such a highly catalytic one-pot method for the generation of homoallyl ethers. This procedure works well with a variety of aldehydes. Both dimethyl and diethyl acetals (entry 6) could be generated easily and converted to the corresponding homoallyl ethers.

The allylation reaction proceeded rapidly and smoothly at room temperature in all cases. In contrast, the use of harsher Lewis acid catalysts such as TiCl_4 requires inconveniently low temperatures (-78°C) for the allylation reaction.¹ Acetals derived from ketones reacted sluggishly with allyltrimethylsilane. In a few trial runs with cyclohexanone and acetophenone, the expected homoallyl ether did form, but significant amounts of unreacted ketone remained (>30%). Although with time (24 h) the ketone was slowly converted to the homoallyl ether, indicating that an equilibrium exists between the ketone and acetal, the allylation reaction never reached completion.

During the course of developing the sequential one-pot allylation method with aldehydes, we found that even if acetal formation was not complete (ca. 70% complete as determined by GC analysis), high yields of the homoallyl ether were obtained upon addition of the allyltrimethylsilane. This observation suggested that the reaction of the acetal with allyltrimethylsilane shifts the

TABLE 2. Bismuth Triflate Catalyzed Three-Component Synthesis of Homoallyl Ethers Using Trialkylorthoformates^a

Entry	Substrate	Product	Time	Yield ^b (%)
1 ^c	PhCHO		1 h 40 min	80
2 ^c	<i>p</i> -ClC ₆ H ₄ CHO		50 min	79
3 ^d	<i>p</i> -CH ₃ C ₆ H ₄ CHO		45 min	77
4 ^d			1 h 15 min	82
5 ^d			30 min	79
6			2 h 30 min	27 ²
7 ^{c,e}	C ₉ H ₁₉ CHO		1 h	80
8 ^c			18 h	40

^a Reaction conditions: 2 equiv of trialkylorthoformate and 2 equiv of allyltrimethylsilane were used. ^b Refers to yield of isolated, purified product. Yields are not optimized. The purity of all products was determined to be 96–99% by ¹H and ¹³C NMR spectroscopy and GC analysis unless otherwise mentioned. Superscript against yield refers to literature reference for the product. ^c Reaction was carried out with 5.0 mol % of $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$. ^d Reaction was carried out with 2.0 mol % of $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$. ^e Product was determined to be 94% pure by GC and NMR spectroscopy. Remainder was starting material.

aldehyde–acetal equilibrium toward acetal formation, which subsequently undergoes rapid allylation. This observation prompted us to investigate a three-component, one-pot method for the conversion of aldehydes to homoallyl ethers.²³ These results are summarized in Table 2. This method involves stirring the aldehyde, trialkylorthoformate, and allyltrimethylsilane in the presence of $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ in CH_3CN . The reaction is rapid and gives moderate to good yields of the homoallyl ether (Table 2). A control experiment revealed that the reaction of allyltrimethylsilane with aldehydes under the reaction conditions is very slow. Although allyltrimethylsilane does react with trialkylorthoformates, the success of the three-component method indicates that the conversion of the aldehyde to the acetal is the fastest reaction in the pot and the acetal in turn undergoes rapid allylation. Although the method worked with the aromatic conjugated aldehyde, cinnamaldehyde (entry 5), the attempted conversion of *trans*-2-hexenal (entry 6) to the corresponding homoallyl ethyl ether gave poor yields.

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TABLE 3. Bismuth Triflate Catalyzed Three-Component Synthesis of Homoallyl Ethers Using Alkoxytrimethylsilanes

Entry	Substrate	R ² OSiMe ₃ (equivalents) ^a	mol % Bi(OTf) ₃ ·xH ₂ O	Product	Time	Yield (%) ^b
1a	PhCHO	R ² = Me (1.2 equiv)	0.1		45 min	78
1b	<i>m</i> -BrC ₆ H ₄ CHO	R ² = Me (2.0 equiv) ^c	0.1		2 h	81 ³⁰
1c	<i>p</i> -ClC ₆ H ₄ CHO	R ² = Me (1.2 equiv)	0.5		3 h	74
2a	<i>m</i> -BrC ₆ H ₄ CHO	R ² = Et (1.9 equiv)	0.1		3 h	82 ¹⁵
3a	PhCHO	R ² = PhCH ₂ (1.2 equiv)	1.0		40 min	80 ¹⁸
3b	<i>p</i> -BrC ₆ H ₄ CHO	R ² = PhCH ₂ (1.2 equiv)	1.0		1 h	57 ¹⁸
3c	<i>m</i> -MeC ₆ H ₄ CHO	R ² = PhCH ₂ (1.2 equiv)	1.0		40 min	76 ¹⁸
3d	(CH ₃) ₃ CCHO	R ² = PhCH ₂ (1.2 equiv) ^d	3.0		30 min	42 ¹⁸
4a	PhCHO	R ² = Allyl (1.2 equiv)	1.0		1 h 35 min	71 ²⁴
4b	<i>p</i> -ClC ₆ H ₄ CHO	R ² = Allyl (1.7 equiv) ^e	1.0		2.5 h	69 ²⁴

^a Reactions were carried out using 1.2 equiv of allyltrimethylsilane unless otherwise mentioned. ^b Refers to yield of isolated, purified product. Yields are not optimized. The purity of all products was determined to be 96–99% by ¹H and ¹³C NMR spectroscopy and GC analysis. Superscript numbers refer to the literature reference for the product. ^c Reaction was carried out using 2.0 equiv of allyltrimethylsilane. ^d Reaction was carried out neat. ^e Reaction was carried out using 1.7 equiv of allyltrimethylsilane.

Even after 2.5 h, the crude product contained significant amounts of unreacted starting material (20%) in addition to several unidentifiable products that contained olefinic protons as indicated by NMR analysis. The desired homoallyl ether product was obtained in low yield after flash chromatography. Similar results have been reported with the use of AlCl₃ or BF₃·Et₂O as a catalyst.² The low yields were attributed to the formation of polymeric material. Again, it was not possible to achieve high conversion with ketones. With cyclohexanone, after 18 h, the corresponding homoallyl ether was obtained in a 40% yield after chromatographic purification. With acetophenone, less than 40% product formed after 24 h.

One drawback of the method outlined in Table 2 is that only a few trialkylorthoformates are commercially available, thus limiting the type of homoallyl ether that can be synthesized by this method. Hence, we investigated the utility of alkoxytrimethylsilanes to achieve similar transformations. This approach to generating homoallyl ethers presents several advantages. A wide range of alkoxytrimethylsilanes is commercially available. Also, we were able to carry out the reaction with 0.1–1.0 mol % bismuth triflate instead of 2.0–5.0 mol % required in the procedure using trialkylorthoformates (Table 2). The versatility of this method can be seen from the results presented in Table 3. A wide variety of homoallyl ethers

TABLE 4. Three-Component Method for the Conversion of Aldehydes to Homoallyl Acetates Using Bi(OTf)₃·xH₂O as a Catalyst^a

Entry	Aldehyde	Product	Time	Yield ^b (%)
1	PhCHO		1 h	66 ²⁶
2	<i>p</i> -ClC ₆ H ₄ CHO		12 h	57 ²⁶
3	<i>p</i> -CH ₃ C ₆ H ₄ CHO		1 h	59 ²⁶
4	<i>m</i> -CH ₃ OC ₆ H ₄ CHO		2 h 15 min	59 ²⁶
5	<i>p</i> -CH ₃ OC ₆ H ₄ CHO		1 h	63 ²⁶

^a Reaction conditions: 3 equiv of acetic anhydride and 2 equiv of allyltrimethylsilane were used. ^b Refers to yield of isolated, purified product. Superscript numbers refer to the literature reference for the product.

including allyl, benzyl, ethyl, and methyl ethers could be synthesized. Homoallyl benzyl ethers allow functional group manipulation at the alkene as well as at the benzyl group, whereas homoallyl alkyl ethers are somewhat inert at the ether functionality. The formation of homoallyl benzyl ethers from aliphatic aldehydes (Table 3, entry 3d) did not give high yields. Although the aldehyde was consumed in <1 h, purification of the crude product by flash chromatography gave only 30–45% yield of the desired product. Similar results were obtained with heptanal and decanal.

Homoallyl allyl ethers can serve as useful precursors to cyclic enol ethers via ring-closing metathesis reactions.²⁴ Hence, a simple method for their synthesis is quite desirable. Entries 4a and 4b (Table 3) illustrate the synthesis of two such compounds. The three-component synthesis did not work well with ketones, and even after extended reaction times (48 h), the product mixture was found to be a mixture of unreacted ketone, acetal, and the desired product. It was not possible to exceed 50% conversion even with increased catalyst loading or increased equivalents (2.0) of the allyltrimethylsilane and the alkoxytrimethylsilane.

The conversion of acylals (1,1-diester) to homoallyl esters has been reported in the literature. At least three approaches to the one-pot synthesis of homoallyl acetates from aldehydes are possible. One approach consists of converting the aldehyde to the homoallyl alcohol followed by acylation.²⁵ A second approach would be to convert the aldehyde to the corresponding acylal (1,1-diester) and then react it with allyltrimethylsilane. A third approach, which we report here, consists of a three-component synthesis of homoallyl acetates starting with aromatic aldehydes and catalyzed by Bi(OTf)₃·xH₂O (Table 4). Such

an approach using Sc(OTf)₃ as the catalyst has been reported by Aggarwal and co-workers.²⁶ The success of this method again relies on the fact that the allylation of aldehydes under the reaction conditions is slow. Thus, the aldehyde is first converted to the acylal which then leads to the homoallyl acetate. Confirming this, we detected the intermediacy of an acylal in these reactions by NMR spectroscopy.²⁷ The low yields are a consequence of diallylation that occurs as a side reaction. In fact, with aldehydes containing a strongly electron-donating group such as *p*-MeO (entry 5, Table 4), the major product was one resulting from diallylation. With a conjugated aldehyde such as cinnamaldehyde, the reaction gave a complex mixture consisting of unreacted starting material, acylal, as well as mono- and diallylation product. With aliphatic aldehydes, the reaction did not proceed to any significant extent at all. Although we have previously reported that acylals can be generated easily from aliphatic aldehydes under solvent-free conditions, the attempted one-pot synthesis of homoallyl acetates from aldehydes under solvent free conditions did not work. When the acylal generated from heptanal was reacted with allyltrimethylsilane, even after 24 h, very little homoallyl acetate formed (<10% as indicated by NMR analysis). The remainder was a mixture of unreacted acylal and aldehyde. The aldehyde is presumably obtained by deprotection of the acylal catalyzed by bismuth triflate during the prolonged reaction time.

Conclusions

In summary, three highly catalytic, one-pot methods for the conversion of aldehydes to homoallyl ethers have been developed using bismuth triflate as a catalyst. A one-pot method for the conversion of aldehydes to homoallyl acetates has also been developed. The advantages of these methods include the use of an easy to handle, nontoxic catalyst and the generation of the homoallyl ether or acetate in one step.

Experimental Section

Representative Procedure for the One-Pot Synthesis of a Homoallyl Ether from an Aldehyde. A solution of benzaldehyde (2.00 g, 18.85 mmol) and trimethylorthoformate (3.00 g, 28.28 mmol, 1.5 equiv) in anhydrous CH₃OH (6 mL) was stirred at rt as Bi(OTf)₃·xH₂O (12.3 mg, 0.1 mol %) was added. The reaction mixture was heated at reflux under N₂, and the reaction progress was monitored by GC analysis. When acetal formation was >95% (1 h), the reaction mixture was cooled and methanol was removed on a rotary evaporator. Anhydrous acetonitrile (20 mL) was added to the pot residue followed by addition of allyltrimethylsilane (3.66 g, 32.05 mmol, 2 equiv) and Bi(OTf)₃·xH₂O (0.1237 g, 1.0 mol %). The reaction was stirred for 10 min at rt, and then solid Na₂CO₃ (0.5 g) was added and the mixture was stirred for 15 min. The

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mixture was filtered, and the solids were rinsed with ether (10 mL). The combined filtrates were concentrated on a rotary evaporator to yield the crude product which was purified by filtration through a short plug of silica gel (5% EtOAc/hexanes) to afford the homoallyl ether as a colorless oil (2.29 g, 75%, >99% pure by ^1H and ^{13}C NMR spectroscopy and GC analysis).

Representative Procedure for One-Pot Three-Component Synthesis of a Homoallyl Ether from an Aldehyde Using a Trialkylorthoformate. A solution of piperonal (0.502 g, 3.33 mmol) in CH_3CN (5 mL) was stirred at rt as $\text{HC}(\text{OMe})_3$ (0.707 g, 6.66 mmol), allyltrimethylsilane (0.761 g, 6.66 mmol), and $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ (0.044 g, 0.067 mmol) were added. The solution turned red and, over time, became colorless. After 75 min, solid Na_2CO_3 (1.0 g) was added, and the mixture was stirred for 10 min. The reaction mixture was filtered, and the solids were rinsed with ether (10 mL). The combined filtrates were removed on a rotary evaporator to yield 0.625 g of a colorless liquid. The crude product was purified by flash chromatography on 30 g of silica gel (10% EtOAc/hexanes) to yield the homoallyl ether product as a colorless liquid (0.56 g, 82%, >98% by ^1H and ^{13}C NMR spectroscopy and GC analysis).

Representative Procedure for One-Pot Three-Component Synthesis of a Homoallyl Ether from an Aldehyde Using Alkoxytrimethylsilanes. A solution of benzaldehyde (0.5020 g, 4.72 mmol) in CH_2Cl_2 (10 mL) was stirred at 0 °C as benzyloxytrimethylsilane (1.020 g, 1.1 mL, 5.66 mmol), allyltrimethylsilane (0.6470 g, 0.90 mL, 5.66 mmol), and $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ (0.0310 g, 0.0472 mmol) were added. After 40 min, the reaction mixture was diluted with CH_2Cl_2 (20 mL), and the organic layer was washed with 10% aqueous Na_2CO_3 (15 mL), saturated NaCl (15 mL) and dried (Na_2SO_4). The solvent was removed on a rotary evaporator to yield 1.2746 g of the crude product, which was purified by flash chromatog-

raphy on 70 g silica (5% EtOAc/hexane) to yield the homoallyl benzyl ether as a clear colorless liquid (0.8976 g, 80% yield, >98% by ^1H and ^{13}C NMR spectroscopy and GC analysis).

Representative Procedure for One-Pot Three-Component Synthesis of a Homoallyl Acetate from an Aldehyde. A solution of benzaldehyde (0.5123 g, 4.828 mmol), acetic anhydride (1.479 g, 14.493 mmol), and allyltrimethylsilane (1.099 g, 1.53 mL, 9.627 mmol) in anhydrous acetonitrile (5.0 mL) was stirred under N_2 as $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ (0.1605 g, 0.2446 mmol, 5.0 mol %) was added. After 1 h, aqueous 10% Na_2CO_3 (15 mL) was added to the reaction and the mixture was stirred for 15 min. The reaction mixture was extracted with EtOAc (2 × 20 mL) and washed with water (3 × 15 mL). The organic layer was washed with aqueous saturated NaCl (15 mL) and dried (Na_2SO_4). The solvents were removed on a rotary evaporator to yield an orange liquid that was purified by flash chromatography on 10 g of silica gel (5% EtOAc/hexanes) to yield the homoallyl acetate as a colorless oil (0.6065 g, 66%, >98% by ^1H and ^{13}C NMR spectroscopy and GC analysis).

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Supporting Information Available: General Experimental Section and spectral data (^1H and ^{13}C NMR spectra) for all compounds whose spectral data has not been previously reported in the literature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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